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Cd, Zn, Ni and Cu in the Indian Ocean

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Abstract—Vertical profiles of dissolved Cd, Zn, Ni and Cu in the Northwest Indian Ocean (Arabian Sea) exhibit a nutrient type distribution also observed in other oceans. The area is characterized by strong seasonal upwelling and a broad oxygen minimum zone in intermediate waters. However, neither Cd, Zn, Ni nor Cu appear to be affected by the reducing conditions, in contrast with earlier reported observations of Mn, Fe and rare earth elements.

Low Cd/PO_4 slopes in surface waters of about 0.15 nM/μM are in good agreement with slopes typical of surface waters in other oceans. Deep water slopes, however, increase from 0.5 nM/μM to 0.85 nM/μM going inshore. These slopes are much higher than published for the deep North Atlantic and North Pacific Oceans, yet comparable to the high Cd/PO_4 slope recently published for the Antarctic Ocean. Deep water cadmium–phosphate *ratios* increase with the age of the deep water from the Atlantic through the Antarctic and Indian to the Pacific Ocean. Slopes of Zn/Si (0.062 nM/μM) are about the same as found in the Pacific Ocean, deep water *ratios* are about 30% higher. The slopes Ni/Si (0.054 nM/μM) are in good agreement with previous reports from the Indian Ocean. The Cu profile shows evidence of surface water inputs, regeneration in intermediate and deep waters and benthic fluxes, and is further influenced by intensive scavenging, notably in surface waters.

INTRODUCTION

IN the North Pacific and North Atlantic Oceans the vertical distributions of dissolved Cd, Zn, Ni and Cu in seawater have been shown to be more or less related to the dissolved major nutrients nitrate, phosphate and silicate (BRULAND, 1983). Deep-water concentrations of these trace metals generally increase with the age of deep water going from the North Atlantic to the East Pacific Ocean. At any given station the correlation between Cd and phosphate is usually very tight (BOYLE, 1988; Table 1). The dataset for Zn is much smaller, but its relation with dissolved silicate is convincing as well (BRULAND, 1980; BRULAND and FRANKS, 1983; Table 2). For Ni a correlation with both phosphate and silicate has been suggested from North Pacific observations (SCLATER *et al.*, 1976; BRULAND, 1980; JONES and MURRAY, 1984; Table 3). In the (northwest) Indian Ocean DANIELSSON (1980) found a good relationship only with silicate. North Atlantic distributions of Ni only vaguely resemble the nutrient type increase with depth (BRULAND and FRANKS, 1983; JICKELLS and BURTON, 1988), where occasionally a modest correlation with

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Table 1. *Relation between dissolved* Cd *and* PO_4 *in the oceans*: Cd (nM) = a PO_4 (μM) + b, *where* a = *slope* Cd–PO_4 *relation*; b = *intercept* Cd–PO_4 *relation*; r = *coefficient of correlation*; *and* n = *number of samples*

Lat.	Long.	*a*	*b*	*r*	*n*	Depth range	Authors
Arctic Ocean							
82.31°N	43.57°E	0.14	0.08		10	0–2400	DANIELSSON and WESTERLUND (1983)
Atlantic Ocean (NW)							
34.06°N	66.07°W	0.25	−0.02	0.99	11	0–2962	BRULAND and FRANKS (1983)
Southern Ocean							
57.00°S	49.00°W	0.63	−0.76	0.91	30	0–4000	NOLTING and DE BAAR (1990)
60.46°S	63.26°W	0.65	−0.85	0.99	10	0–1850	MARTIN *et al.* (1990)
Indian Ocean (NW)							
14.30°N	67.00°E	0.50	−0.49	0.97	14	100–4000	This study
14.30°N	67.00°E	0.15	−0.05	1.0	4	0–100	This study
		offshore					
21.16°N	63.22°E	0.50	−0.46	0.97	10	30–3360	This study
22.30°N	60.40°E	0.87	−1.26	0.96	10	50–3000	This study
22.30°N	60.40°E	0.16	−0.01	0.97	5	0–50	This study
		inshore					
Pacific Ocean (S)							
52.50°S	178.05°W	0.58	−0.41	0.88	19	0–5271	BOYLE *et al.* (1976)
Pacific Ocean (N)							
~35.00°N	~130.00°W	0.35	−0.07	0.99	34	0–5000	BRULAND (1980)
		(three stations)					
30.34°N	170.36°W	0.29	0.05	0.94	21	0–5446	BOYLE *et al.* (1976)

either phosphate (DANIELSSON *et al.*, 1985) or silicate (YEATS and CAMPBELL, 1983) is suggested. In the Arctic Ocean Ni does not resemble nutrient elements at all (YEATS, 1988). At first glance the vertical distribution of Cu resembles that of silicate (BOYLE *et al.*, 1977; BRULAND, 1980; BRULAND and FRANKS, 1983), yet upon close inspection Cu deviates

Table 2. *Relation between dissolved* Zn *and* Si *in the oceans. Symbols are the same as in Table* 1

Lat.	Long.	*a*(Si)	*b*	*r*	*n*	Depth range	Authors
Atlantic Ocean							
45.00–53.00°N	35.00–41.00°W	0.17	2.3	0.71	>50	0–4310	YEATS and CAMPBELL (1983)
34.06°N	66.07°W	0.09	0.27	0.84	10	0–2962	BRULAND and FRANKS (1983)
Indian Ocean							
all stations		0.06	0.50	0.89	50	0–4000	This study
14.30°N	67.00°E	0.09	−0.33	0.91	12	175–2500	This study
21.16°N	63.22°E	0.06	1.37	0.86	10	0–1200	This study
22.30°N	60.40°E	0.05	1.31	0.92	17	0–3000	This study
23.30°N	59.00°E	0.05	0.50	0.89	19	0–2750	This study
Pacific Ocean							
37.05°N	123.22°W	0.06	−0.18	0.99	10	0–2950	BRULAND *et al.* (1978b)
32.00–37.00°N	122.00–144°W	0.05	0.02	1.0	>50	0–4875	BRULAND (1980)

Table 3. Relation between dissolved Ni, PO_4 *and* Si *in the oceans. Symbols are the same as in Table 1*

		Ni[nM] = aPO$_4$[μM] + bSi[μM] + c or Ni[nM] = aPO$_4$[μM] + c or Ni[nM] = bSi[μM] + c						
Lat.	Long.	a(PO$_4$)	b(Si)	c	r	n	Depth range	Authors
Atlantic Ocean								
10.00°S–60.00°N	36.00–0.00°W	4.2		1.52	0.34	>50	surface	KREMLING (1985)
40.00–59.00°N	15.00–20.00°W	1.44		1.94	0.94	23	0–2800	DANIELSSON *et al.* (1985)
				(four stations)				
34.06°N	66.07°W	2.8		2.00	0.982	9	0–2962	BRULAND and FRANKS (1983)
45.00–53.00°N	35.00–41.00°W	1.5		2.20	0.886	65	0–4310	YEARS and CAMPBELL (1983)
			0.063	3.3	0.684			(Si only)
		1.2	0.019	2.2	0.896			(Combined Si and PO$_4$)
				(three stations)				
Indian Ocean								
2.43°N	66.02°E;		0.048	5.2	0.92	19	0–3132	DANIELSSON (1980)
19.01°N	67.01°E							
All stations			0.054	2.45	0.944	>50	0–4000	This study
14.30°N	67°E		0.048	2.50	0.949	16	0–4000	This study
19.00°N	67°E		0.074	2.57	0.971	19	0–3200	This study
21.16°N	63.22°E		0.050	3.03	0.950	17	0–3363	This study
22.30°N	60.40°E		0.053	2.44	0.977	20	0–3000	This study
23.30°N	59.00°E		0.064	1.91	0.987	20	0–2750	This study
Pacific Ocean								
16.32°N	123.01°W	1.08	0.036	3.3	0.94	21	0–4187	SCLATER *et al.* (1976)
			0.072	3.8	0.98	11	0–1200	With Si only
31.23°N	150.02°W	0.98	0.030	3.7	0.94	12	0–4939	SCLATER *et al.* (1976)
			0.043	4.4	0.957	12		With Si only
177.2°N	53.7°W	0.38	0.020	4.8	—	16	0–3711	BOYLE *et al.* (1981)
			0.027	4.7	0.905	16		With Si only
175.5°N	52.4°W	1.88	0.009	2.5		19	0–5271	Same
32.00–37°N	122.00–144°W	0.95	0.033	2.74	0.995	>50	0–4875	BRULAND (1980)
				(three stations)				

Table 4. Relation between dissolved Cu *and* Si *in the oceans. Symbols are the same as in Table* 1

Lat.	Long.	*a*(Si)	*b*	*r*	*n*	Depth range	Authors
Atlantic Ocean							
~35.00°N	~64.5°W	0.049	1.02	0.78	21	0–3900	JICKELLS and BURTON (1988)
34.00°N	66.00°W	0.041	1.12	0.93	10	0–2962	BRULAND and FRANKS (1983)
53.39°N	71.53°W	0.044	0.82	0.90	11	500–3000	HANSON *et al.* (1988); Si from SAKAMOTO-ARNOLD *et al.* (1978)
Southern Ocean							
57.00°S	49.00°W	0.024	0.59	0.19	19	100–4000	NOLTING and DE BAAR (1990)
60.46°S	63.26°W	0.012	0.84	0.96	10	0–1850	MARTIN *et al.* (1990)
Indian Ocean							
~0–20.00°N	~68.00°E	0.024	0.73	0.94	15	150–3000	DANIELSSON (1980)
22.30°N	60.40°E	0.019	−0.13	0.95	9	250–3000	This study
Pacific Ocean							
52.40°S	178.00°W	0.021	1.11	0.914	19	0–5257	BOYLE *et al.* (1977)
42.31°N	144.59°W	0.012	0.73	0.95	7	0–1000	BRULAND (1980)
50.00°N	145.00°W	0.006	1.56	0.90	16	0–1500	MARTIN *et al.* (1990)

significantly from silicate as it is also strongly influenced by local input sources in surface and bottom waters, combined with intensive scavenging throughout the water column (Table 4).

Zn and Cu are essential to phytoplankton growth, and such biochemical functionality would provide an elegant explanation of the relations with major nutrients in seawater (REDFIELD *et al.*, 1963; MOREL and HUDSON, 1985). However, the observed correlations between metals (Cd, Zn, Ni, Cu) and nutrients more commonly have been explained by the adsorptive 'scavenging' removal of trace metals from surface waters along with settling biogenic particles (GOLDBERG, 1954; CRAIG, 1974; SCHINDLER, 1975; TUREKIAN, 1977; BALISTRIERI *et al.*, 1981; HONEYMAN *et al.*, 1988; SHERRELL, 1989). Here one would expect considerable spatial and temporal variability of the active scavenging particles, their size distribution, surface properties and settling characteristics. When assuming major control by such adsorptive mechanism the ensuing metal–nutrient relations, notably for Cd/phosphate, appear rather fortuitous. Recently PRICE and MOREL (1990) reported that in Zn-depleted surface waters Cd may be utilized instead of Zn by phytoplankton, the first evidence towards a biochemical functionality of Cd as explaining the Cd/phosphate relation in seawater.

More important for the open ocean proper, one recognizes that the above general relationships are based largely on observations in the North Pacific and North Atlantic basins only. Reports of dissolved trace metals have been very scanty for the Indian Ocean (DANIELSSON, 1980), and for that matter, the entire Southern or Antarctic Ocean (BOYLE *et al.*, 1976, 1977; ORREN and MONTEIRO, 1985; BORDIN *et al.*, 1987; NOLTING and DE BAAR, 1990; MARTIN *et al.*, 1990).

The relationship between these metals and nutrients usually breaks down in shallow marginal seas and semi-enclosed basins such as the Mediterranean (BOYLE *et al.*, 1985). Inadequate deep water renewal rates in more restricted basins may lead to anoxic

conditions. Upon anoxia the concentrations of dissolved Cu, Cd and Zn decrease dramatically as a result of sulfide (co)precipitation, with major shifts in inorganic complexation (BYRNE *et al.*, 1988) of the metal remaining in solution (JACOBS *et al.*, 1985, 1987; HARALDSSON and WESTERLUND, 1988). The concentration of Ni in anoxic waters is usually not affected by redox processes (HARALDSSON and WESTERLUND, 1988; JACOBS *et al.*, 1985).

Here we report trace metal distributions in the Northwest Indian Ocean (Arabian Sea) which is characterized by highly productive upwelling waters overlying an extensive oxygen minimum zone. Oxidation–reduction reactions were previously shown to control the distributions of Fe, Mn (SAAGER *et al.*, 1989) and the Rare Earth Elements (GERMAN *et al.*, 1990).

SAMPLING AND METHODS

The NERC/IMER cruise aboard U.K. R.V. *Charles Darwin* took place in August–October 1986. It ran northward along 67°E across the equator into the Arabian Sea (Stas 1–6), then westward into the Gulf of Oman (Stas 6–11) (Fig. 1). Here we present Cd results for Stas 5, 7 and 8, Zn results for Stas 5, 6, 8 and 9 and Ni and Cu results for Stas 5–9.

Samples were collected using a new stainless steel CTD-rosette sampler with modified (BRULAND *et al.*, 1979) precleaned 10-l Teflon-coated Go-Flo bottles (General Oceanics). The rosette sampler was first sent down to obtain real-time hydrographic data and to flush the Go-Flo bottles. Upon recovery, the samples, taken during the upcast, were pressure-filtered through acid-cleaned 0.4 μm Nuclepore filters using in-line all-Teflon filtration units, acidified with 0.25 ml quartz distilled HCl (Q-HCl) to pH 2–3, and stored in hot-acid cleaned 250 ml polyethylene bottles. The filters were not kept for analysis. The data thus only include dissolved Cd, Zn, Ni and Cu as defined by the 0.4 μm filter. It is expected, however, that more than 90% of the trace metal content will be present in the dissolved fraction (SHERRELL, 1989). Trace metals were preconcentrated ashore, using Chelex-100 (BioRad) ion-exchange chromatography (KINGSTON *et al.*, 1979) modified after DE BAAR (1983). In addition, seawater samples from Sta. 7 were analysed for Cd using APDC/DDDC-chloroform extraction (BRULAND *et al.*, 1979). Milli-Q water (Millipore) and Q-distilled reagents were used throughout the procedure.

Concentrates were analysed with a Perkin–Elmer 5000 atomic absorption spectrophotometer equipped with Zeeman background correction (FERNANDEZ *et al.*, 1980), an HGA-400 heated graphite furnace and AS-40 autosampler. Standard addition was used to correct for matrix interference. Several batches of 1000 ppm stock solutions were purchased from Merck® and intercalibrated to verify their overall accuracy, found to be within the reproducibility of the GFAAS method. Furthermore exchange of standard solutions between Free University lab and NIOZ lab confirmed the above accuracy. Reagent blanks were assessed beforehand and found to be negligible or below detection limit. Overall procedural blanks were assessed by extracting Milli-Q water (Ni, Zn and Cu) or reagents only (Cd) and amounted to 0.3 nM for Ni, 0.1 nM for Cu, 0.2 nM for Zn and below detection limit for Cd. Concentrations were corrected for blanks. Both at sea and shore analytical procedures were performed in a class-100 laminar flow bench situated inside a clean air van or laboratory. Detection limits were 0.15 nM for Ni, 0.06 nM for Cu, 0.1 nM for Zn and 0.005 nM for Cd. Precision of the measurements was about 5% for Ni, Cu and Cd at 2 nM, 1 nM and 0.5 nM, respectively and 10% for Zn.

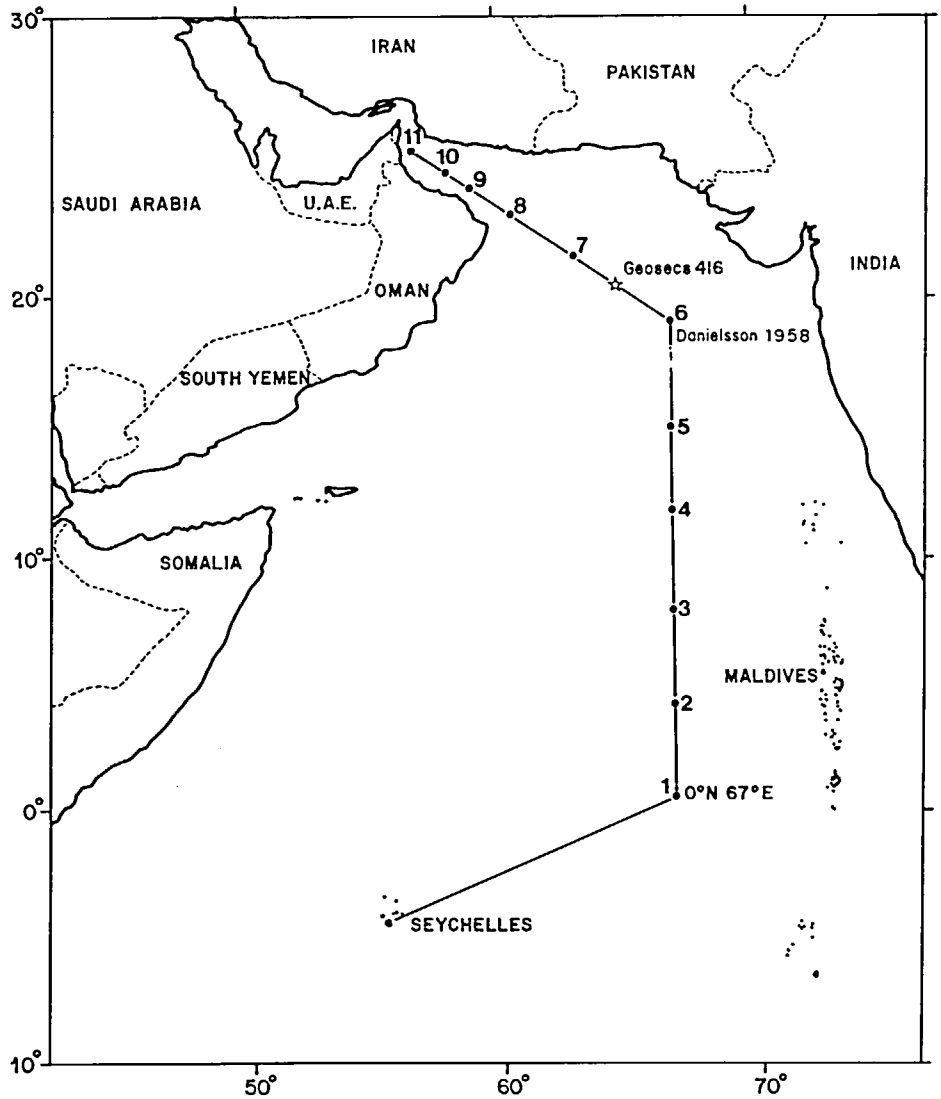


Fig. 1. Sampling locations in the Northwest Indian Ocean: Sta. 5 (14°30'N, 67°E); Sta. 6 (19°N, 67°E); Sta. 7 (21°16'N, 63°22'E); Sta. 8 (22°30'N, 60°40'E); Sta. 9 (23°30'N, 50'E). Also shown are Stas 416 of GEOSECS and 1958 of DANIELSSON (1980).

HYDROGRAPHY

The Northwest Indian Ocean, or more specifically the Arabian Sea, is characterized by strong seasonal upwelling driven by southwest monsoons (April–September) (SLATER and KROOPNICK, 1982; SEN GUPTA and NAQVI, 1984). The ample supply of nutrients caused by the strong upwelling leads to an impressive primary production averaging twice that of the world's oceans (SLATER and KROOPNICK, 1982; ITTEKOT *et al.*, 1988). Intense remineralization in the intermediate waters drives the efficient consumption of available dissolved oxygen. The Arabian Sea is a semi-enclosed basin due to the near presence of the Asian

continent, while the Carlsberg ridge also has been suggested to restrict circulation (SLATER and KROOPNICK, 1982). The Arabian Sea oxygen minimum results from a combination of excessive *in situ* consumption combined with oxygen depletion in the renewal water before it reaches the Arabian Sea (SWALLOW, 1984). Modern estimates of the residence time of the oxygen depleted layer are 2–4 years (NAQVI, 1987; SOMASUNDAR and NAQVI, 1988), instead of earlier estimates of 30 years (SLATER and KROOPNICK, 1982; SEN GUPTA and NAQVI, 1984). Such rapid circulation prevents complete anoxia (NAQVI, 1987).

In the Arabian Sea the oxygen minimum zone reportedly extends roughly between 100 and 1200 m depth, with concentrations as low as 1 μM (DEUSER *et al.*, 1978; SLATER and KROOPNICK, 1982; SEN GUPTA and NAQVI, 1984). At all our stations the low oxygen layer was found at this depth range with concentrations as low as 6 μM (Fig. 2, Table 5). At the inshore Stas 8 and 9 the presence of Arabian Gulf (formerly Persian Gulf) overflow waters was evident from maxima in temperature, salinity and oxygen content (Fig. 2, Table 5), in good agreement with earlier observations (SEN GUPTA and NAQVI, 1984).

Intense denitrification with ensuing nitrate depletion has been reported previously (NAQVI, 1987), but complete anoxia does not occur in the water column (DEUSER *et al.*, 1978). Curiously, highest rates of denitrification have been reported for more open waters where primary production is much lower than in the coastal upwelling area off Oman (NAQVI, 1987; SOMASUNDAR and NAQVI, 1988). At our inshore Stas 7, 8 and 9, where upwelling and productivity were highest, the nitrate depletion was stronger than at offshore Stas 5 and 6 (Fig. 3, Table 5). In contrast, the nitrite maximum, present between 170 and 600 m depth was most developed at the offshore Stas 5 and 6, in keeping with above earlier reported highest rates of denitrification.

The oxygen minimum also appears to affect the distribution of phosphate, judging from the concentration minimum found between 100 and 300 m depth, most pronounced at the inshore stations (Fig. 4, Table 5). Within completely anoxic basins such discontinuities of dissolved phosphate are more dramatic but still poorly understood (BREWER and MURRAY, 1973; FONSELIUS, 1974; SHAFFER, 1986; CODISPOTI *et al.*, 1989). The vertical distribution of silicate apparently is not influenced by the oxygen minimum. (Fig. 4, Table 5). Nutrient distributions were found to be in good agreement with GEOSECS 416 (19°45'N, 64°37'E, occupied in 1977), suggesting minor fluctuations within one decade.

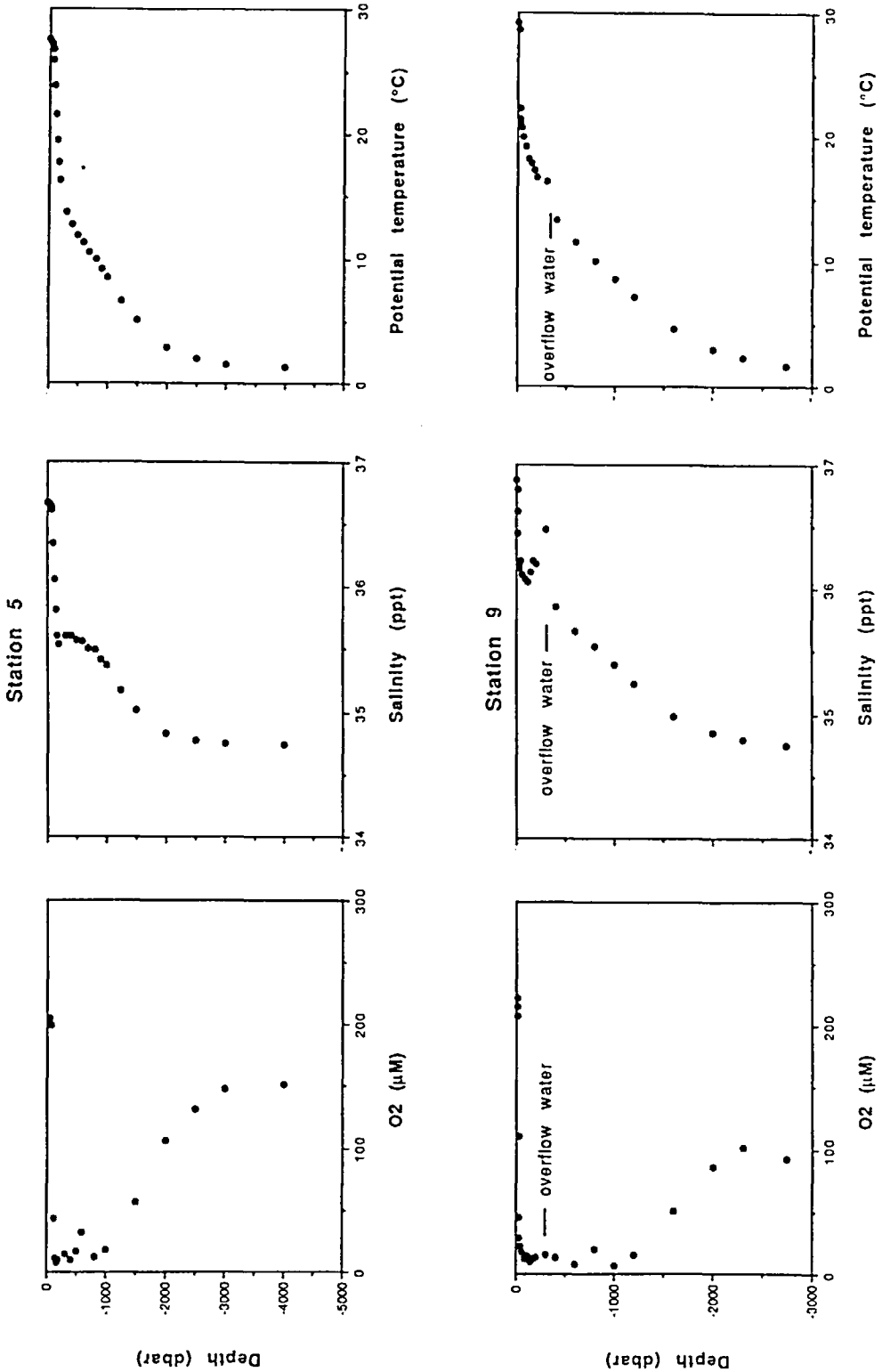
The vertical gradients of the nutrients (nutricline) were less steep in an offshore direction, consistent with a general decrease in productivity. This trend was strongest for nitrate and least pronounced for silicate. At inshore Sta. 9 concentrations of phosphate and nitrate increased most strongly in the upper 50 m, whereas at Sta. 5 the strongest gradient was observed over the first 175 m.

RESULTS AND DISCUSSION

Cadmium

At first sight the vertical distribution of dissolved Cd at Stas 5, 7 and 8 (Fig. 5, Table 5) was very similar to that of phosphate. On closer inspection the two distributions differ significantly.

The surface water depletion for Cd was much more pronounced than for phosphate and more closely resembled that of nitrate. At Sta. 8, which is located right in the highly productive upwelling zone off Oman, the surface water Cd concentration was about


Station 5
Station 9
Depth (dbar)
O2 (µM)
Salinity (ppt)
Potential temperature (°C)
overflow water

80 pM. The concentration then increased by almost one order of magnitude in the upper 100 m to about 0.7 nM. Phosphate concentrations increased less, from 0.6 μM at the surface to some 2.3 μM at 100 m depth. Nitrate concentrations increased from about 1 μM to about 25 μM. Between 100 and 250 m depth Cd and phosphate appeared to be decoupled. Cadmium concentrations had a minimum at 125 m depth, then gradually increased to a maximum value of 1.1 nM at 1200 m depth and decreased to bottom water values of 0.85 nM. For phosphate a minimum of 2.16 μM was present between 100 and 250 m depth, then the concentration increased to 2.75 μM at 1200 m depth, then decreased towards the sea floor.

At Sta. 5, located in the centre of the basin, surface water Cd concentrations were only 8 pM, one order of magnitude less than at Sta. 8. Our Sta. 5 is located near Sta. 1958 of DANIELSSON (1980) (Fig. 1) where much higher surface water Cd values were reported. At our station the concentration increased by almost two orders of magnitude to 0.6 nM at 200 m depth. At the surface phosphate concentrations were still 0.4 μM and increased sharply to about 2.1 μM over the first 200 m, only a factor of 5, about the same as was observed at Sta. 8. Nitrate concentrations, like those of Cd, increased by more than two orders of magnitude over the same depth range. Below 200 m depth the concentrations of Cd and phosphate gradually increased to some 0.8 nM Cd and 2.6 μM PO_4 between 1200 and 1500 m depth. This maximum Cd concentration is in perfect agreement with the data reported by DANIELSSON (1980), who found a maximum of 0.8 nM at about the same depth at his Sta. 1958. Both Cd and phosphate concentrations slightly decreased again towards the sea floor.

The Cd-distribution at Sta. 7 is similar to those observed at Stas 5 and 8, concentrations and trends generally plotting between those at latter stations, in agreement with other hydrographical observations such as surface water nutrient concentrations. Deep water Cd concentrations at Sta. 8 (1080 pM) were about 23% higher than at Sta. 5 (830 pM), the difference for phosphate was only 6%.

At Stas 5, 7 and 8 a modest Cd minimum can be distinguished at the top of the suboxic zone (Fig. 5, Table 5), just below the onset of denitrification judging from the nitrate anomaly (Fig. 3, Table 5). At Sta. 5 the onset of the nitrate anomaly (at 200 m) and the Cd minimum (0.60 pM at 300 m depth), respectively are located deeper than at Sta. 8 (NO_3 at 100 m; Cd = 0.55–0.65 nM at 125–150 m depth), where both are more pronounced. For Sta. 7 the anomalies fall in between these two stations. This might hint at some relation hitherto not reported for reducing environments. However, the Cd minima also appear to be associated with the presence of Arabian Gulf overflow waters (Table 5), suggesting them to be merely an advective feature, analogous to maxima of dissolved Mn at Stas 8 and 9 (SAAGER *et al.*, 1989).

The well documented correlation between dissolved Cd and phosphate in other oceans (BOYLE *et al.*, 1976; BRULAND *et al.*, 1978a; BRULAND, 1980) was also found in the north west Indian Ocean, but is not entirely straightforward (Fig. 6). The earlier reported discontinuity between surface waters and deep waters (BOYLE, 1988) was especially pronounced at Stas 5 and 8. The lack of a similar discontinuity at Sta. 7 is mainly due to the small amount of surface water data. For surface waters down to 100–150 m depth

Fig. 2. Vertical profiles of dissolved oxygen, salinity and potential temperature (θ) for Stas 5 and 9. The presence of Arabian Gulf overflow water is indicated at Sta. 9.

(approximate depth of thermocline) an excellent Cd/PO_4 correlation existed with Cd/PO_4 slopes of 0.15–0.16 nM/μM at both stations. Presumably such low slopes are commonly found in ocean surface waters (BOYLE, 1988; KREMLING and POHL, 1989).

For water below the thermocline the correlation was highly significant, but Cd/PO_4 slopes differ greatly between stations: 0.5 nM/μM at Stas 5 and 7 and 0.87 nM/μM at Sta. 8, respectively. These deep-water slopes are much higher than previously reported for other

Table 5. Seawater analysis results and associated hydrographic data for Stas 5–9. Preliminary results for Cd reported previously (DE BAAR et al., 1987) showed similar trends but are rejected due to then unforeseen matrix interference problems. Therefore samples for Stas 5, 7 and 8 were reanalysed with two different techniques. Dissolved oxygen was analysed on board ship by triplicate Winkler titrations

Depth (dbar)	PO_4 (μM)	H_4SiO_4 (μM)	NO_3 (μM)	NO_2 (μM)	Temp. (°C)	Sal. (‰)	Sigma-*t*	O_2 (μM)	Cd (pM)	Zn (nM)	Ni (nM)	Cu (nM)
Station 5												
4	0.42	4.92	d.l	d.l	27.594	36.673	23.789	n.a	7.5	n.a	n.a	n.a
20	0.41	3.82	0.38	d.l	27.353	36.668	23.863	n.a	8.4	n.a	n.a	n.a
40	0.42	4.92	d.l	d.l	27.245	36.659	23.891	205.3	n.a	n.a	2.09	1.42
60	0.45	4.74	0.61	d.l	26.814	36.631	24.008	199.4	n.a	n.a	2.16	4.18
80	0.66	4.92	4.72	d.l	25.858	36.609	24.294	n.a	47	n.a	n.a	n.a
100	1.11	10.2	12.9	d.l	23.955	36.351	24.680	n.a	114	5.00	n.a	n.a
125	1.67	16.8	21.6	d.l	21.627	36.057	25.128	43.5	n.a	n.a	3.32	2.35
150	1.93	22.6	24.0	d.l	19.453	35.810	25.524	11.1	n.a	n.a	3.29	1.85
175	2.04	27.3	22.8	1.95	17.704	35.605	25.809	8.0	535	1.40	3.72	1.78
200	2.11	32.1	21.1	3.26	16.261	35.544	26.107	10.5	613	n.a	4.27	1.43
300	2.21	37.9	24.0	2.81	13.761	35.602	26.703	14.1	596	2.48	3.52	1.52
400	2.27	42.8	26.9	0.1	12.698	35.606	26.924	9.9	664	2.91	3.81	1.20
500	2.35	50.6	28.1	d.l	11.814	35.576	27.073	16.7	719	2.96	6.03	2.01
600	2.40	52.8	28.1	d.l	11.278	35.565	27.165	32.6	728	5.76	5.70	2.02
700	2.44	59.5	30.1	d.l	10.530	35.511	27.259	n.a	724	4.01	5.85	1.49
800	2.47	66.3	31.2	d.l	9.950	35.491	27.344	12.6	722	8.23	6.63	3.50
900	2.51	72.8	31.9	d.l	9.153	35.413	27.417	n.a	760	3.89	n.a	n.a
1000	2.53	n.a	33.5	d.l	8.535	35.372	27.484	17.2	763	4.30	3.67	1.79
1250	2.58	94.7	34.5	d.l	6.680	35.171	27.598	n.a	828	8.45	n.a	n.a
1500	2.56	110.2	34.9	d.l	5.099	35.021	27.680	56.3	829	10.1	7.03	3.15
2000	2.39	130.6	33.8	d.l	2.857	34.832	27.764	105.9	731	10.6	8.42	n.a
2500	2.28	135.7	32.7	d.l	1.999	34.775	27.792	131.8	667	9.85	7.96	3.53
3000	2.21	136.8	32.3	d.l	1.577	34.750	27.804	148.8	728	c.s	7.69	3.18
4000	2.15	137.7	32.0	d.l	1.374	34.741	27.811	151.3	605	c.s	9.90	4.94
Station 6												
10	0.35	2.33	d.l	d.l	n.a	n.a	n.a	206.8	n.a	n.a	2.25	1.09
20	0.36	2.19	d.l	d.l	27.229	36.681	23.913	207.9	n.a	n.a	2.58	1.39
30	0.42	2.19	d.l	d.l	26.407	36.599	24.114	209.2	n.a	n.a	2.53	1.86
40	0.38	2.74	d.l	d.l	26.316	36.620	24.158	206.1	n.a	n.a	2.35	1.76
50	0.44	2.60	1.13	d.l	26.195	36.646	24.216	n.a	n.a	n.a	n.a	n.a
70	0.70	4.38	6.36	d.l	25.335	36.547	24.410	161.1	n.a	n.a	2.21	1.38
90	1.20	9.17	17.7	d.l	22.436	36.305	25.087	74.8	n.a	n.a	2.82	2.48
120	1.43	11.1	20.0	d.l	21.309	36.204	25.327	55.9	n.a	n.a	4.30	1.91
150	1.62	15.9	22.2	d.l	19.504	36.043	25.689	37.1	n.a	n.a	4.80	2.01
175	1.74	19.0	20.6	d.l	18.364	35.970	25.926	17.4	n.a	n.a	5.47	2.18
204	1.70	22.7	18.7	1.19	17.018	35.966	26.252	15.4	n.a	n.a	3.64	1.89
300	1.84	27.5	20.7	2.92	14.543	35.882	26.753	8.8	n.a	n.a	4.36	0.91
400	1.94	32.4	23.1	1.51	13.388	35.810	26.942	24.8	n.a	n.a	4.95	1.22
500	1.97	37.4	26.4	d.l	12.168	35.655	27.066	7.5	n.a	n.a	5.02	1.34
600	2.03	43.0	28.6	d.l	11.434	35.606	27.168	12.6	n.a	n.a	6.58	1.66
800	2.10	54.9	31.6	d.l	10.129	35.534	27.347	6.3	n.a	n.a	7.10	1.79
1000	2.19	66.3	34.6	d.l	8.680	35.400	27.483	15.3	n.a	n.a	7.01	1.26
1200	2.30	76.5	36.3	d.l	7.272	35.247	27.575	20.0	n.a	n.a	7.95	1.68
1600	2.22	97.2	36.5	d.l	4.676	34.994	27.708	58.8	n.a	n.a	8.44	2.03
2000	2.08	109.1	35.3	d.l	2.979	34.847	27.765	94.5	n.a	n.a	9.87	2.39
2500	1.97	116.4	34.5	d.l	2.008	34.778	27.793	118.8	n.a	n.a	12.3	c.s
3200	1.92	119.3	33.8	d.l	1.490	34.746	27.807	134.2	n.a	n.a	11.8	7.63

d.l. = Concentration below detection limit.

n.a. = Not analysed.

c.s. = Contamination suspected to such extent that data is deemed not reliable.

Table 5. continued

Depth (dbar)	PO_4 (μM)	H_4SiO_4 (μM)	NO_3 (μM)	NO_2 (μM)	Temp. (°C)	Sal. (%)	Sigma-*t*	O_2 (μM)	Cd (pM)	Zn (nM)	Ni (nM)	Cu (nM)
Station 7												
4.2	0.48	3.35	0.57	d.l	26.861	36.389	23.811	233.7	n.a	n.a	2.90	2.44
10	0.47	3.24	0.71	d.l	26.724	36.377	23.846	n.a	n.a	n.a	n.a	n.a
20	0.59	3.38	1.79	0.07	26.477	36.335	23.893	222.0	n.a	2.83	2.68	1.29
30	0.97	5.41	7.50	0.78	24.765	36.107	24.252	n.a	47.,46	n.a	n.a	n.a
40	1.31	6.91	15.4	0.07	23.269	36.095	24.688	n.a	n.a	n.a	n.a	n.a
50	1.37	6.69	16.8	d.l	23.216	36.254	24.824	131.0	n.a	n.a	4.64	1.66
60	1.59	9.51	20.8	0.07	21.799	36.127	25.132	n.a	256.,259	n.a	n.a	n.a
80	1.72	13.3	22.1	d.l	21.181	36.170	25.336	41.4	n.a	3.91	3.04	1.51
100	1.87	15.4	22.8	d.l	20.647	36.196	25.502	28.2	493	n.a	3.42	1.69
125	2.10	20.0	18.4	d.l	19.285	36.083	25.777	13.9	557.,543	n.a	5.43	c.s
150	2.02	22.3	21.3	d.l	18.685	36.101	25.945	n.a	n.a	n.a	n.a	n.a
175	1.96	22.7	20.6	d.l	18.291	36.170	26.097	14.7	612.,619	2.43	2.21	1.33
200	2.18	27.9	19.7	d.l	17.839	36.237	26.261	17.7	556.,614	1.63	4.14	1.15
285	2.20	29.2	19.6	d.l	16.710	36.414	26.670	n.a	n.a	3.07	4.93	1.36
400	2.40	42.9	20.6	0.43	13.740	35.932	26.963	12.7	766.,788	3.68	5.84	1.41
600	2.58	58.4	25.6	0.14	11.494	35.649	27.190	10.5	n.a	3.78	5.59	3.84
800	2.69	73.4	30.1	d.l	9.931	35.523	27.373	14.1	838.,948	4.50	6.98	1.39
1000	2.79	91.8	30.4	d.l	8.325	35.368	27.514	15.1	941.,1021	8.82	8.23	1.54
1200	2.82	101.3	34.4	d.l	6.965	35.223	27.600	21.5	n.a	8.87	9.06	1.70
1600	2.92	127.4	34.5	d.l	4.394	34.969	27.720	62.6	830.,795	n.a	9.64	3.49
2000	2.65	142.4	33.9	d.l	2.923	34.845	27.769	90.8	n.a	n.a	8.44	2.59
2500	2.54	150.4	33.1	d.l	1.974	34.774	27.793	117.0	n.a	n.a	10.7	c.s
3360	2.39	156.1	32.6	d.l	1.462	34.744	27.807	127.4	841.,864	n.a	11.0	n.a
Station 8												
3.0	0.58	3.85	1.00	0.07	n.a	n.a	n.a	219.0	n.a	0.96	2.63	2.22
5.1	0.58	3.56	0.86	0.07	25.671	36.572	24.325	222.2	104	n.a	2.40	3.26
10.3	0.61	3.03	0.93	0.07	25.661	36.570	24.326	221.5	82	2.78	2.85	2.48
14.4	0.58	4.31	1.07	0.07	25.666	36.574	24.328	221.7	86	2.60	2.62	2.00
19.8	0.90	5.66	4.57	0.29	24.445	36.263	24.466	203.9	130	3.03	3.10	2.30
30.4	1.42	7.97	12.0	1.14	21.947	35.855	24.884	159.1	180	1.33	3.09	1.27
50.4	1.91	10.5	20.4	0.14	20.774	35.888	25.233	109.3	320	2.33	3.06	1.07
74.6	2.23	17.1	25.8	0.07	19.394	35.813	25.542	48.1	680	2.57	3.61	1.68
100	2.26	23.1	24.7	0.50	18.269	35.765	25.792	11.4	710	1.22	3.84	1.05
124.4	2.16	25.1	23.1	0.42	17.330	35.737	26.002	16.1	550	2.59	4.28	c.s
150	2.16	27.1	22.6	0.29	16.577	35.731	26.177	12.7	670	1.30	4.01	1.41
176	2.16	28.6	23.0	0.14	16.022	35.794	26.354	16.3	n.a	n.a	4.29	0.71
200	2.16	31.4	22.1	0.07	15.746	35.856	26.465	n.a	720	2.70	4.46	1.04
240	2.16	33.0	21.8	0.07	15.196	35.911	26.632	8.1	750	2.95	3.57	0.75
400	2.36	45.5	23.9	0.36	12.860	35.770	27.109	16.5	850	3.54	4.26	0.81
600	2.49	60.8	26.0	0.42	11.277	35.630	27.216	10.9	970	n.a	4.77	0.95
800	2.58	73.6	29.6	0.21	10.043	35.531	27.360	12.6	1020	4.52	5.41	1.38
1000	2.68	87.8	31.9	0.14	8.664	35.400	27.485	13.0	1040	4.46	6.58	1.27
1200	2.74	102.1	33.3	d.l	7.149	35.239	27.587	24.4	1080	6.11	7.75	1.44
1600	2.71	128.7	33.7	d.l	4.566	34.985	27.713	55.1	n.a	n.a	9.03	2.42
2000	2.55	144.6	33.0	d.l	2.944	34.845	27.767	88.6	1000	n.a	n.a	2.47
2500	2.45	152.1	32.1	d.l	1.965	34.770	27.791	111.0	n.a	n.a	11.7	3.20
3000	2.39	155.2	31.4	d.l	1.589	34.744	27.798	118.7	880	11.0	n.a	6.74
Station 9												
4.6	0.43	3.36	d.l	d.l	29.251	36.875	23.390	n.a	n.a	n.a	4.2	3.86
9.3	0.46	3.85	d.l	0.04	28.701	36.799	23.518	216.2	n.a	0.81	2.78	2.71
15	0.57	4.63	1.23	0.11	n.a	36.620	n.a	222.2	n.a	n.a	3.07	2.16
20	0.82	6.68	3.69	0.69	n.a	36.448	n.a	207.7	n.a	n.a	3.81	2.36
25	1.53	10.5	16.0	0.84	22.373	36.169	25.002	110.7	n.a	n.a	1.56	1.43
30	1.86	12.3	22.5	0.29	21.430	36.188	25.281	45.8	n.a	n.a	1.99	1.35
35	1.93	14.1	22.9	0.12	21.220	36.207	25.354	29.0	n.a	1.94	1.63	1.23
45	1.95	14.1	23.0	d.l	20.861	36.228	25.469	21.9	n.a	1.03	2.37	1.10
60	2.07	17.4	22.7	d.l	20.024	36.112	25.605	18.0	n.a	0.92	2.54	1.08
90	2.09	19.4	21.5	d.l	19.210	36.078	25.792	12.7	n.a	1.92	2.35	1.26
120	2.12	22.6	20.2	d.l	18.215	36.057	26.029	14.8	n.a	4.99	2.39	0.95
140	2.10	23.7	19.9	d.l	17.952	36.137	26.156	10.1	n.a	3.67	2.27	1.30
170	2.16	25.9	19.3	d.l	17.392	36.220	26.357	12.2	n.a	1.24	2.76	1.26
200	2.12	26.7	20.0	d.l	16.805	36.208	26.489	13.7	n.a	1.36	2.60	0.79
300	2.13	28.6	20.0	d.l	16.458	36.481	26.781	15.2	n.a	2.49	3.04	0.98
400	2.30	37.7	23.7	d.l	13.409	35.857	26.974	13.5	n.a	1.08	3.62	0.65
600	2.53	51.8	25.6	d.l	11.661	35.664	27.171	7.4	n.a	4.37	4.43	1.01
800	2.62	66.0	30.0	d.l	10.100	35.534	27.352	19.6	n.a	2.57	4.33	0.68
1000	2.72	80.6	32.6	d.l	8.682	35.400	27.482	6.3	n.a	4.38	7.23	0.89
1200	2.79	91.8	34.3	d.l	7.203	35.245	27.583	15.2	n.a	4.63	6.75	1.21
1600	2.79	115.2	34.8	d.l	4.618	34.989	27.711	50.8	n.a	7.51	7.62	1.38
2000	2.58	129.0	33.8	d.l	2.996	34.848	27.764	85.9	n.a	11.4	9.74	2.15
2300	2.53	133.3	33.5	d.l	2.294	34.794	27.782	102.0	n.a	9.40	10.2	2.52
2750	2.52	130.3	33.2	d.l	1.701	34.752	27.796	93.3	n.a	7.65	9.00	2.38

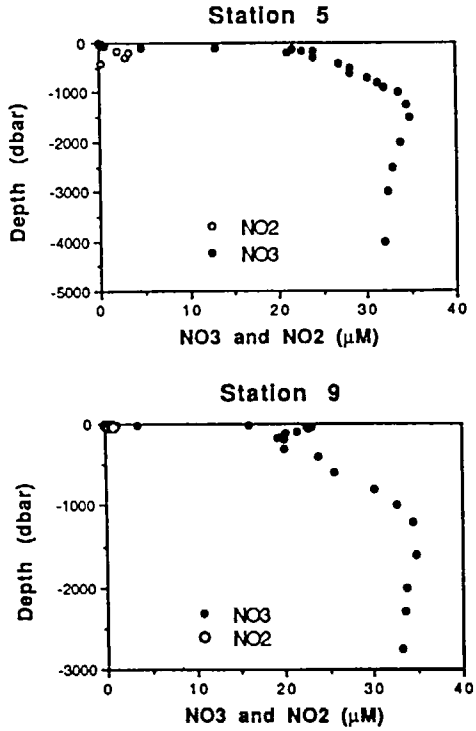


Fig. 3. Vertical profiles of dissolved nitrate and nitrite at Stas 5 and 9.

oceans which do not exceed 0.35–0.4 nM/μM as observed in the North Pacific (Table 1). Until now there has been a concensus that the Cd/PO_4 slope in oceanic deep waters is remarkably uniform globally (BOYLE, 1988). The assumed global slope of about 0.35–0.4 nM/μM in deep waters has also been applied in paleoceanographic reconstructions of deep-water nutrient regimes in ancient oceans (BOYLE, 1988; BROECKER and DENTON, 1989).

At close inspection the presumed global deep water slope of about 0.35–0.4 nM/μM appears to be somewhat of a generalization (Table 1). In the Arctic Ocean the very low slope of about 0.14 nM/μM throughout the water column resembles the value presumably 'typical' of surface waters. Within the Atlantic Ocean there appears to be a tendency towards higher slopes going southward, with values in the northwest Atlantic around 0.24 nM/μM, in the eastern north and equatorial Atlantic around 0.20 nM/μM. Recently NOLTING and DE BAAR (1990) reported high Cd/PO_4 slopes of 0.63 nM/μM for the Atlantic sector of the Antarctic Ocean, consistent with the slope of 0.65 nM/μM derived from a recently published Cd profile in Drake Passage (MARTIN *et al.*, 1990). Similar slopes of 0.65–0.80 nM/μM were also obtained for the Indian sector of the Southern Ocean when applying the Redfield slope NO_3/PO_4 of 16 to earlier reported relations between Cd and nitrate (BORDIN *et al.*, 1987). The one available data set for the south Pacific Ocean (GEOSECS 293, BOYLE *et al.*, 1976) taken on its own value, yields a slope of 0.58 nM/μM throughout the water column, significantly different from the slope of about 0.26–0.36 nM/μM for the various North Pacific data sets (Table 1). A high slope of 0.54 was also

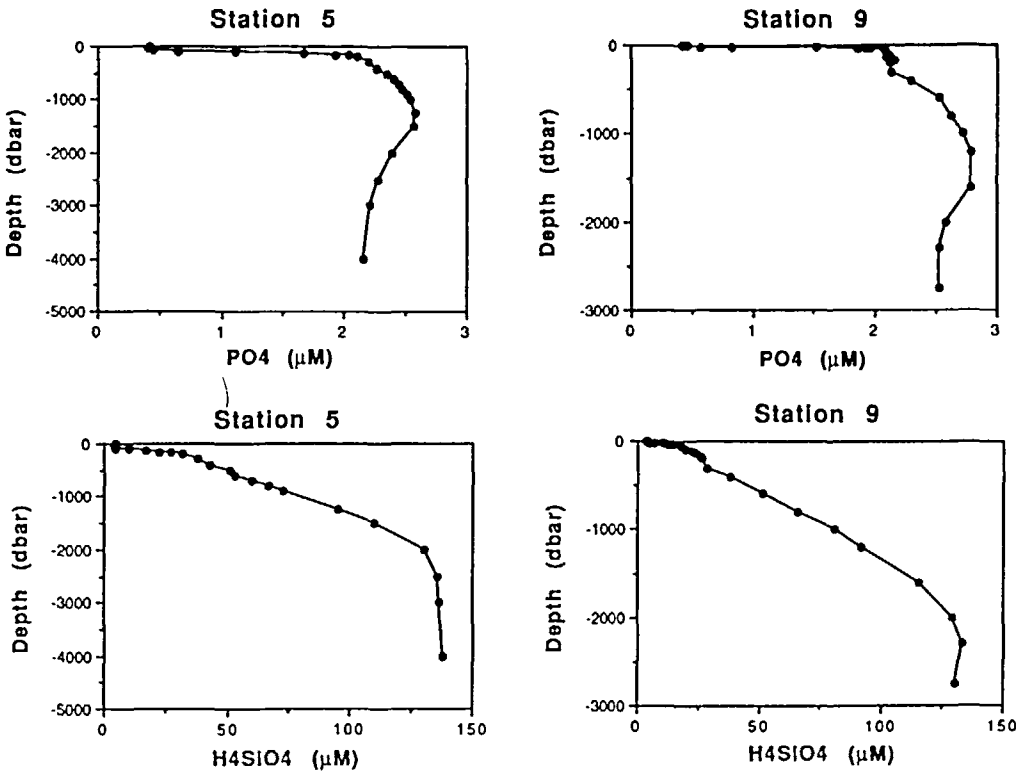


Fig. 4. Vertical profiles of dissolved phosphate and silicate at Stas 5 and 9.

calculated for a suite of stations in the shallow upwelling waters off California (MARTIN *et al.*, 1976).

From our and other observations (Table 1) it is now demonstrated that the concept of one, globally uniform, value for the Cd/PO_4 slope has to be reconsidered, to recognize the significant range in Cd/PO_4 slopes throughout the world ocean and in geological time (DE BAAR *et al.*, submitted).

However, although common practice, correlating properties throughout the vertical water column is in fact a violation of a basic principle of water exchange in the ocean, proceeding predominantly along isopycnals, i.e. horizontally. Since surface and deep waters are separated by a strong density gradient and have totally different renewal time scales, it is not surprising if one observes different slopes in both water masses. From the above discussion it follows that the Cd/phosphate slopes do not show an unambiguous trend. When plotting the Cd/phosphate *ratio* vs depth for each station (Fig. 7 for selected stations) one observes that deep and bottom water ratios increase in a predictable way from the north Atlantic, via the Antarctic to the Pacific, generally with higher values in older waters. A few regions plot outside the general trend, notably our Sta. 8 and GEOSECS Sta. 293 in the southwest Pacific (BOYLE *et al.*, 1976). The deep water Cd/phosphate ratio is probably a function of preformed concentrations, regeneration of both elements during decomposition of organic matter and the general deep-water circulation. Station 8 is located in an anomalous situation with extreme primary productivity, high

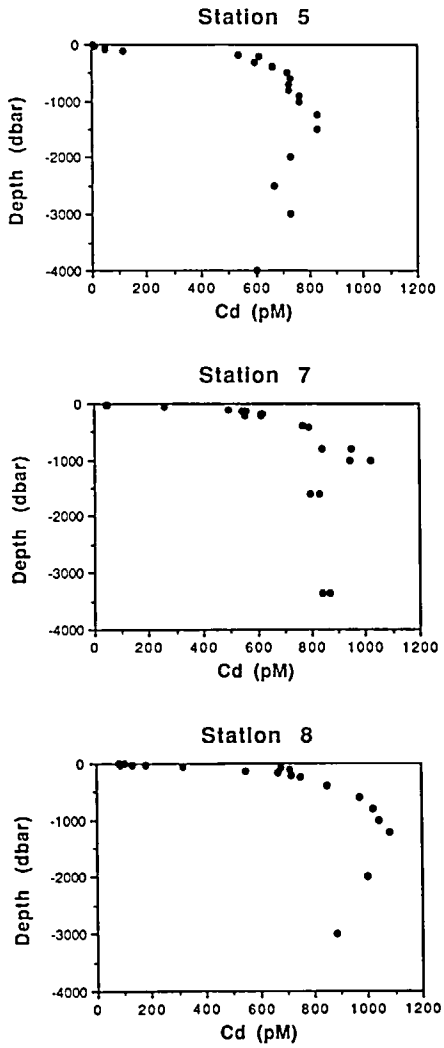


Fig. 5. Vertical profiles of dissolved Cd at Stas 5, 7 and 8. Note different depth scales.

preformed Cd and phosphate and probably restricted circulation (see hydrography). An extensive discussion on the exact mechanisms driving the cadmium phosphate relationship will be the subject of a separate paper (SAAGER *et al.*, in preparation).

Above considerations relying solely on the hydrographic distributions of dissolved Cd and phosphate, provided some insight but did not yield a clue to the possible underlying physico-chemical or biochemical mechanism. Of all trace metals studied, Cd shows the most pronounced surface water depletion. Also, at our stations the concentration difference between surface waters and deep waters is largest for Cd, about two orders of magnitude at Sta. 5. Surface water minima of dissolved Cd in the Pacific and Atlantic Ocean were recently shown to coincide with maxima of particulate Cd, mainly present in organic form (SHERRELL, 1989). This may be ascribed to either adsorption on outer

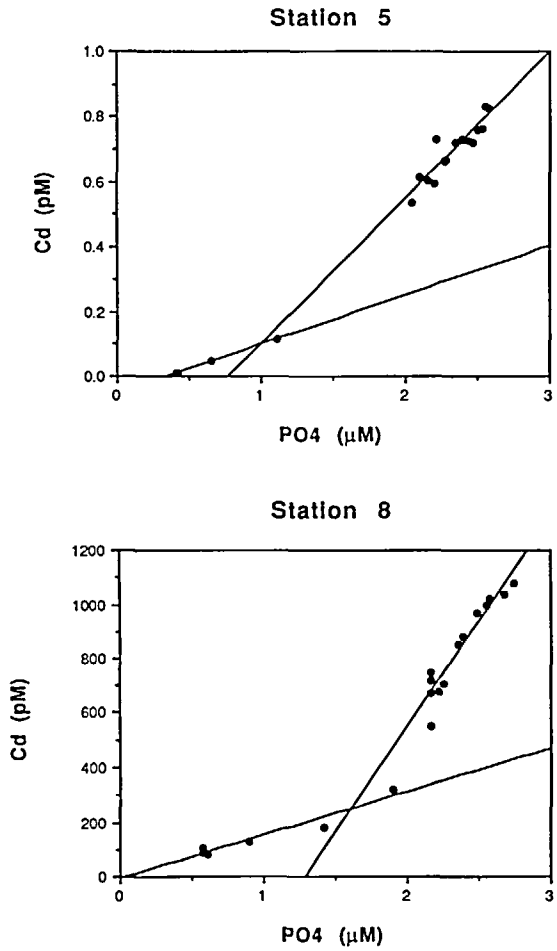


Fig. 6. The relationships between dissolved Cd and phosphate at offshore Sta. 5 and nearshore upwelling Sta. 8. Note the distinct break somewhere between surface and deep waters, as well as the high Cd/PO4 slope in the deep water, see also Table 1.

surfaces of biogenic particles, or true uptake through the cell wall and incorporation in tissue material. Recently PRICE and MOREL (1990) in laboratory experiments found evidence of Cd substitution for Zn in a marine diatom (*Thalassiosira weissflogii*) at very low Zn activities, thus for the first time providing evidence of a biological functionality of Cd in marine algae. At the moment it is not clear whether this would be a mechanism common also for other algal species. Implications for the field have yet to be established. For example in the Arabian Sea, upwelling would bring waters with high concentrations of free ionic Zn to the surface (see below: Zn), so that Cd substitution for Zn may be relatively unimportant at this site.

Zinc

The vertical distribution of Zn (Fig. 8, Table 5) showed low surface water values between 1 and 3 nM. In deeper waters Zn concentrations increased towards the sea floor to

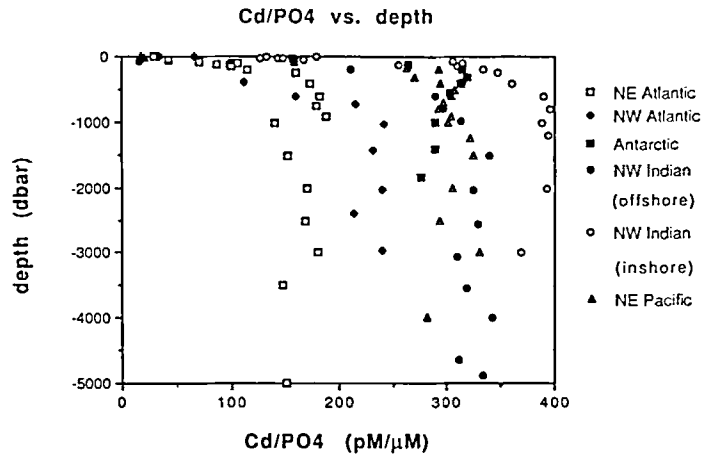


Fig. 7. Cadmium–phosphate ratios vs depth for selected stations from the major ocean basins. Northeast Atlantic values are from unpublished results (SAAGER *et al.*, in preparation), northwest Atlantic values from BRULAND and FRANKS (1983), Antarctic values from MARTIN *et al.* (1990), Indian Ocean are our values and northeast Pacific values from BRULAND (1980).

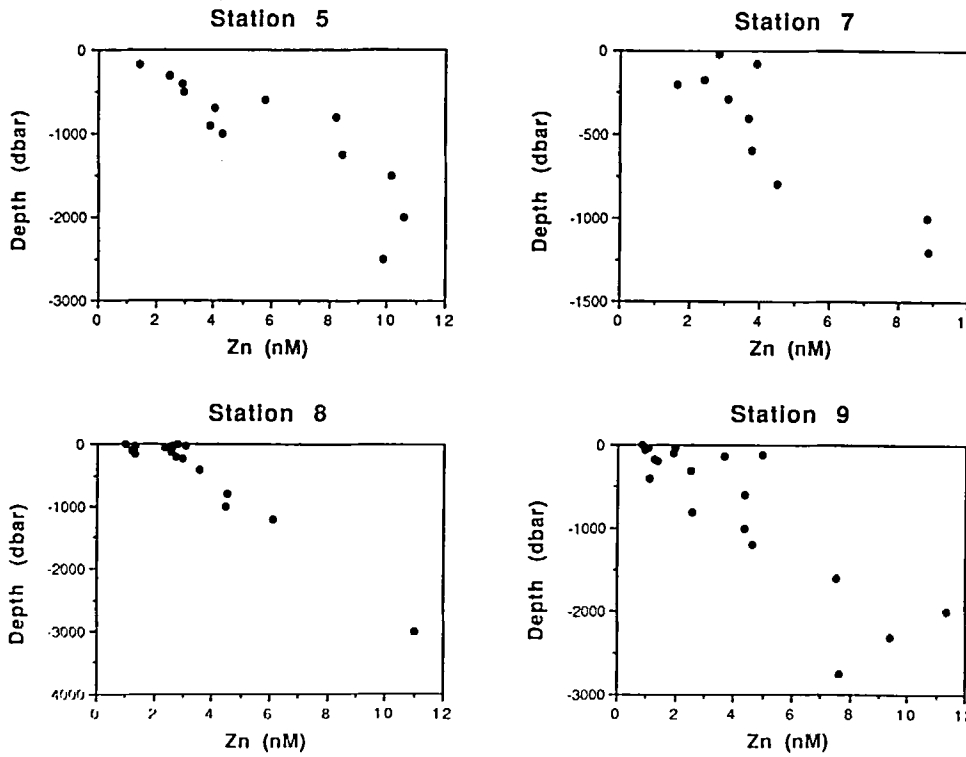


Fig. 8. Vertical profiles of dissolved Zn at Stas 5, 7, 8 and 9. Note different depth scales.

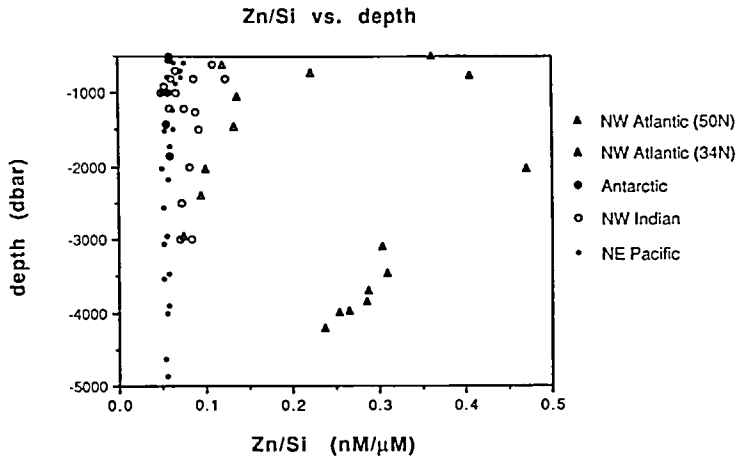


Fig. 9. Zinc–silicate ratios vs depth for selected stations from the major ocean basins. Northwest Atlantic values are from YEATS and CAMPBELL (1983; 50°N) and BRULAND and FRANKS (1983; 34°N), Antarctic data are from MARTIN *et al.* (1990), Indian Ocean our data and northeast Pacific data are from BRULAND (1980).

values between 9 and 12 nM. These values are slightly higher than reported for the north Pacific Ocean (BRULAND *et al.*, 1978b; BRULAND, 1980), in keeping with higher deep water Ni and Cd concentrations found at our stations. The profiles exhibit considerable scatter and the very low surface water values of less than 0.3 nM reported for the north Pacific were not observed. Overall analytical blanks in the laboratory were always low, but some of the scatter may result from contamination during sampling and storage which cannot be ruled out entirely. Presumably for the latter reason the world dataset for Zn is still very limited and only one more or less reliable profile for the Indian Ocean has previously been published (DANIELSSON, 1980). Most reported surface water Zn concentrations fall in the range of our data. In analogy with Fe, significant progress in clean sampling techniques is still warranted in order to arrive at a consistent global dataset of Zn concentrations.

For deep waters of all four stations a significant correlation between dissolved Zn and Si was observed:

$$\text{Zn (nM)} = 1.0 + 0.0616\,\text{Si}\ (\mu\text{M}), \qquad r = 0.88,$$

where the overall Zn/Si slope is very similar to Zn/Si ranging from 0.054 to 0.06 nM/μM as reported for the Pacific Ocean (Table 2). For individual stations the slope varies from 0.051 to 0.085 without any apparent trend (Table 2). Zn/Si slopes found at two stations in the north Atlantic Ocean are higher at 0.086 and 0.17, respectively (Table 2).

Based on the previous considerations (see Cd) we also plotted zinc/silicate ratios vs depth for selected stations (Fig. 9). In agreement with the differential increase of each element with the age of deep water we can see that the Zn/Si ratio in deep waters decreases dramatically from north to south Atlantic, mainly as a result of strongly increasing silicate concentrations towards the south. Surface water concentrations are not discussed since many published surface water concentrations appear contaminated. Antarctic and Pacific ratios are virtually equal (0.05–0.06 nM/μM) but the northwest Indian Ocean is again anomalous in this respect. Plankton species composition combined with deep water

circulation and possibly external deep water sources (e.g. benthic fluxes from pore waters) may all contribute.

Information about surface water Zn concentrations is still very limited, most likely as a result of contamination. This is unfortunate as Zn plays a major role as an essential micronutrient for marine organisms (BRAND *et al.*, 1983; PRICE and MOREL, 1990). Recent investigations (BRULAND, 1989; DONAT and BRULAND, 1990) indicate complexation of Zn with organic ligands to 98%, reducing the free ionic Zn activity to about 2 pM. At these activities various organisms are possibly Zn-limited (BRAND *et al.*, 1983; PRICE and MOREL, 1990). In upwelling areas such as the Arabian Sea deep waters with high free ionic Zn activities (BRULAND, 1989) are brought to the surface so that Zn limitation is unlikely in these waters. This undoubtedly affects the phytoplankton species composition in upwelling waters as compared to oligotrophic gyres.

Nickel

In accordance with previous reports (SCLATER *et al.*, 1976; BOYLE *et al.*, 1981; BRULAND, 1980) surface water concentrations at our stations never reached values lower than 1.5–2 nM in contrast with the pronounced surface water depletion observed for the nutrients (Fig. 10, Table 5). An initial steep increase of Ni over the first few hundred meters to concentrations around 4–5 nM at 500 m depth, was followed by a more gradual increase to concentrations of about 10–12 nM near the sea floor. No concentration changes were observed at the oxygen minimum zone. The profile at Sta. 8 was somewhat different from the other stations. Between 200 and 1000 m depth there was a slight minimum, more or less coincident with the minimum for nitrate. Also, concentrations continued to increase linearly towards the sea floor instead of levelling off as observed at the other stations. In general, deep water Ni concentrations are in very good agreement with previously reported data for this part of the Indian Ocean (DANIELSSON, 1980), but are slightly higher than reported for the Pacific Ocean (SCLATER *et al.*, 1976; BRULAND, 1980; JONES and MURRAY, 1984).

The relation between Ni and the nutrients (Table 3) is not as unequivocal as is the case for Zn and Cd. A good combined correlation of Ni with both phosphate for surface waters as well as silicate for deep waters was observed in the Pacific Ocean (SCLATER *et al.*, 1976; BRULAND, 1980). In the Atlantic Ocean relations are generally less convincing: mostly a convincing correlation with phosphate was found (DANIELSSON *et al.*, 1985; BRULAND and FRANKS, 1983; YEATS and CAMPBELL, 1983), sometimes a reasonable relation with silicate (YEATS and CAMPBELL, 1983), or occasionally a relation with both phosphate and silicate (YEATS and CAMPBELL, 1983). Generally these correlations are less significant than in the Pacific Ocean, and at some Atlantic stations (DANIELSSON *et al.*, 1985) as well as in the Arctic Ocean (YEATS, 1988) there exists no correlation whatsoever. For our five stations in the Indian Ocean a significant correlation between Ni and Si was observed:

$$\text{Ni (nM)} = 2.47 + 0.054\,\text{Si}\ (\mu\text{M}), \qquad r = 0.925$$

in good agreement with the Ni/Si slope of 0.048 nM/μM reported earlier by DANIELSSON (1980) for his Sta. 1958 (Table 3). However the surface water intercept is much lower than the 5.2 nM found by DANIELSSON (1980) and is more similar to the intercepts reported from the Atlantic and Pacific Ocean (Table 3). We found no correlation with phosphate.

Since at our stations only a relation between Ni and silicate was observed (no relation with phosphate was found) we recalculated the relation between Ni and silicate in deep

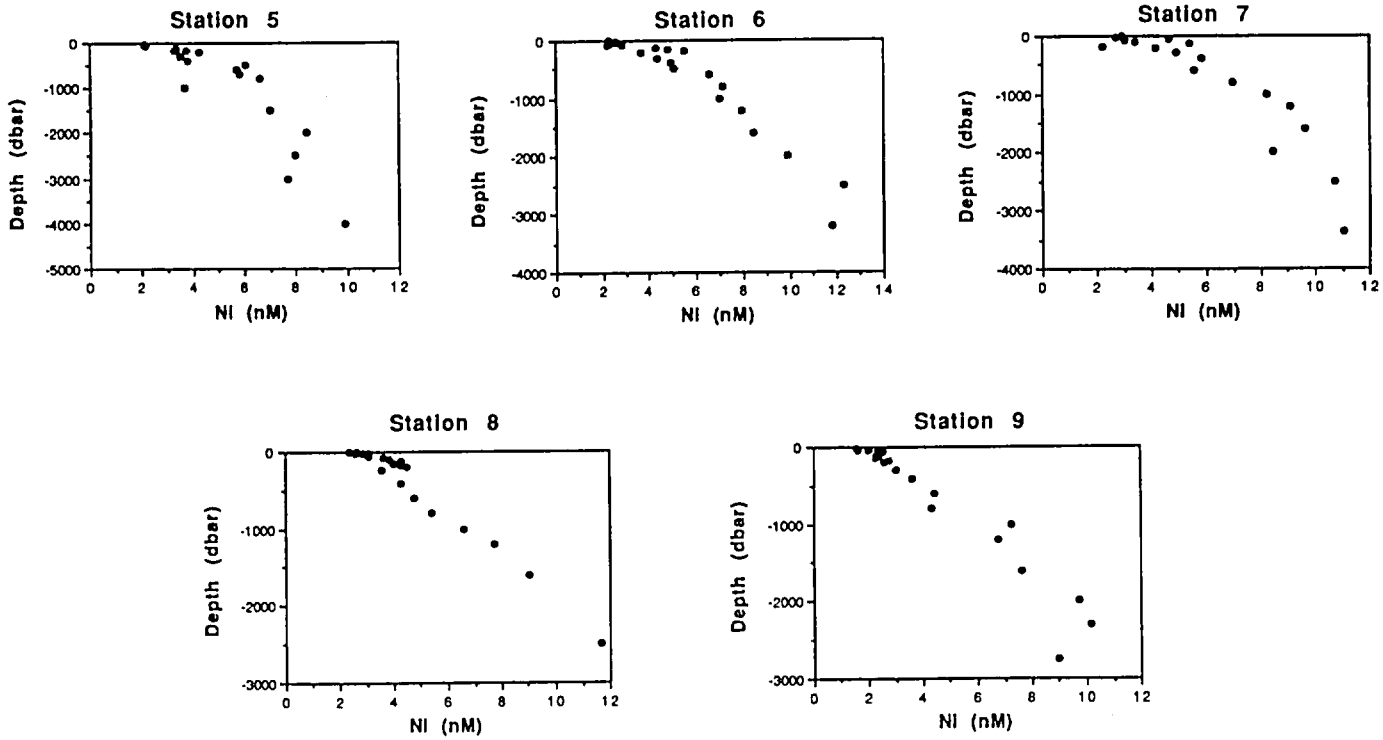


Fig. 10. Vertical profiles of dissolved Ni at Stas 5–9. Note different depth scales.

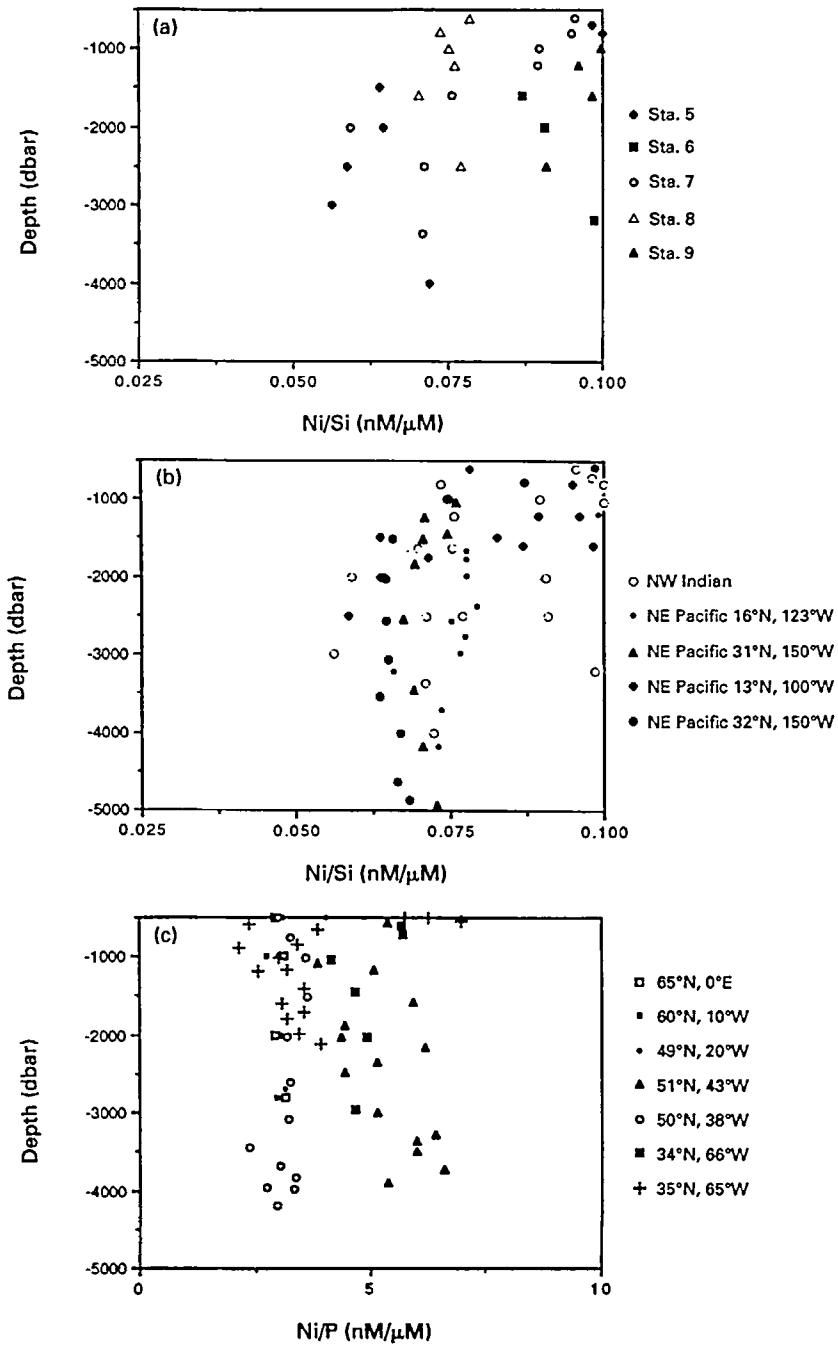


Fig. 11. Nickel–silicate ratios vs depth for (a) Northwest Indian Ocean, (b) stations from the major ocean basins and (c) nickel–phosphate ratios vs depth for the Atlantic Ocean. Data are from SCLATER *et al.* (1976; Atlantic, closed triangles; Pacific, same and closed diamonds), BRULAND (1980; Pacific, closed circles), BOYLE *et al.* (1981; Pacific, small closed diamonds), YEATS and CAMPBELL (1983; Atlantic, open circles), JICKELLS and BURTON (1988; Atlantic, crosses), BRULAND and FRANKS (1983; Atlantic, closed squares) and DANIELSSON *et al.* (1985; Atlantic, open squares, closed squares and small closed diamonds).

water (>1000 m) of other oceans (Table 3). Nickel/silicate slopes do not exhibit a clear trend or if anything slightly decrease from the Atlantic (based on one reference, with only a moderate correlation between Ni and silicate; YEATS and CAMPBELL, 1983) through the Indian to the Pacific Ocean. The combined relation of Ni with phosphate (surface waters) and silicate (deep waters) has been proposed for stations from the Pacific Ocean (SCLATER *et al.*, 1976; BRULAND, 1980; BOYLE *et al.*, 1981). However, when recalculating Ni/silicate correlations for data published by SCLATER *et al.* (1976) and BOYLE *et al.* (1981) a very good correlation between Ni and silicate for *surface* waters is found at one station, whereas at two other stations a similarly significant correlation is only found between Ni and silicate throughout the water column. The concept of the above mentioned combined correlation is not globally valid and local conditions (upwelling where siliceous organisms may dominate phytoplankton species composition, benthic fluxes) probably largely determine to what extent Ni is correlated with either phosphate or silicate. A plot of Ni/phosphate ratios vs depth for the Atlantic Ocean and Ni/silicate ratios vs depth for the Indian and Pacific Oceans does not yield a consistent pattern (Fig. 11). Especially remarkable is the wide range in deep-water Ni/Si ratios found at our stations, which do not exhibit a clear trend.

Copper

The vertical distribution of Cu (Fig. 12, Table 5) showed a pronounced surface water maximum (2–4 nM), which decreased in an offshore direction as was also observed for Mn (SAAGER *et al.*, 1989). In contrast with Cd, Ni and Zn surface water Cu (and Mn) concentrations appear to be strongly influenced by continental (e.g. eolian) sources. Without information on local eolian Cu deposition rates, net fluvial input from the Euphrates, Tigris or Indus or benthic fluxes from near-shore shelf sediments it is not possible to constrain the origin of the surface water enrichment. The strong decrease of Cu in an offshore direction, which was also observed for Mn (SAAGER *et al.*, 1989) combined with the presence of the arid Arabian subcontinent would make a strong eolian source most likely. In remote open ocean waters such surface water enrichment is not observed (BRULAND, 1980; BOYLE *et al.*, 1981; KREMLING, 1985).

Below the surface water maximum concentrations decreased sharply, most likely as a result of particle scavenging, to minimum values between 0.5 and 1.0 nM at about 500 m depth. The Cu concentration further increased more or less linearly to values between 2 and 3 nM in deep waters. Very near the bottom higher concentrations of 5–8 nM were found at three stations, consistent with similar trends for dissolved Mn (SAAGER *et al.*, 1989) and ascribed to a flux derived from reducing sediments (HEGGIE *et al.*, 1987). The interstitial water chemistry of Cu is coupled to the decomposition of organic matter (ELDERFIELD, 1981; SHAW, 1987; GERRINGA, 1990) with high pore water concentrations in sediments with high organic matter content. Shelf sediments in this area contain high concentrations of organic matter (SHIMMIELD *et al.*, 1990) potentially driving benthic Cu fluxes (BOYLE *et al.*, 1981; HEGGIE *et al.*, 1987).

In general the deep water concentrations are in good agreement with previously reported data for the Indian Ocean (DANIELSSON, 1980). Deep-water concentrations are intermediate between Atlantic values of 1.5–3 nM (YEATS and CAMPBELL, 1983; DANIELSSON *et al.*, 1985; JICKELLS and BURTON, 1988) and Pacific values of 4–7 nM (BOYLE *et al.*, 1977; BRULAND, 1980; MOORE, 1981; BRULAND and FRANKS, 1983).

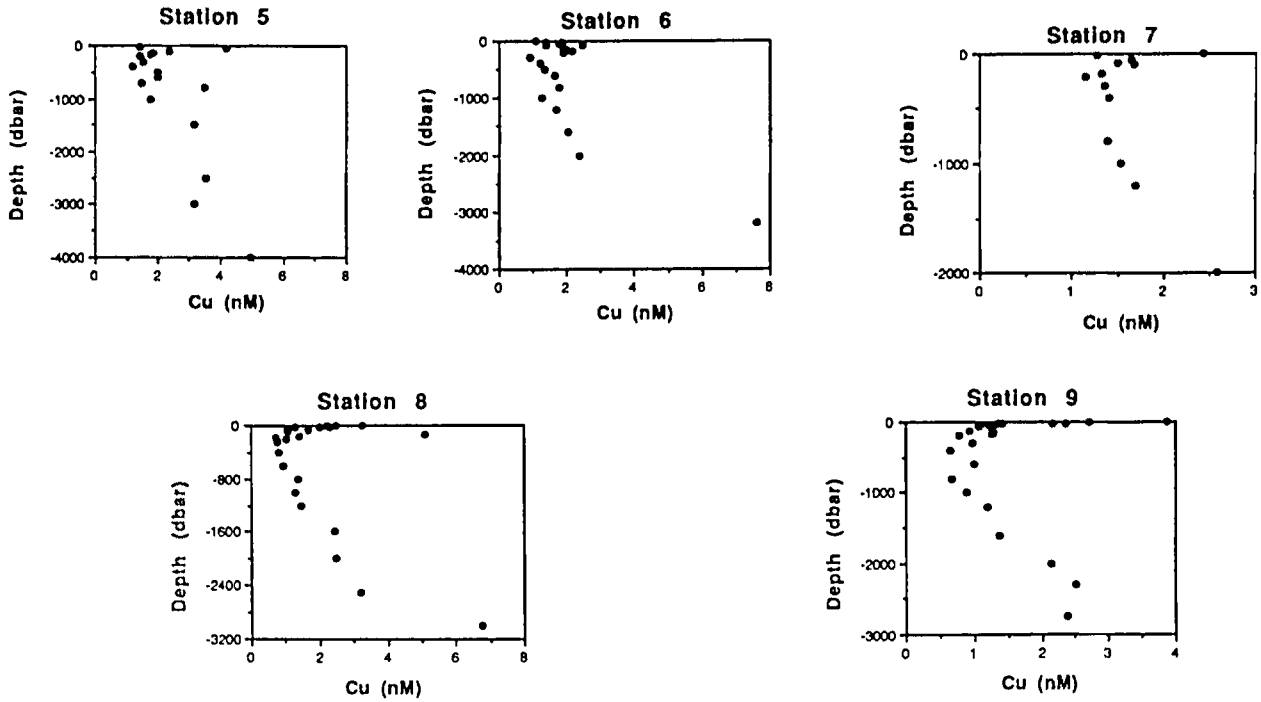


Fig. 12. Vertical profiles of dissolved Cu at Stas 5–9. Note different depth scales.

In deep waters the distribution of Cu resembles that of silicate, with concentrations also increasing from the Atlantic through the Indian to the Pacific Ocean, although Cu/silicate slopes tend to decrease in the same direction, mainly as a result of strongly increasing silicate concentrations. This suggests a common involvement in regeneration cycles. The correlation between Cu and silicate is not unsignificant (Table 4), when taking into consideration that the distribution of Cu is also strongly determined by particle scavenging (BOYLE *et al.*, 1977; BRULAND, 1980). The same type of distribution was reported for the REE in the equatorial Pacific ocean (DE BAAR *et al.*, 1985). In the Indian Ocean the REE are also influenced by redox processes (GERMAN and ELDERFIELD, 1990), presumably indirectly through dissolution of Mn oxide carrier phases.

BOYLE *et al.* (1977) plotted Cu vs potential temperature (θ) for deep waters with a linear θ–salinity relationship. A negative deviation of Cu indicates removal of Cu from the water column by scavenging (CRAIG, 1974). For our stations Cu is plotted against θ for those depth sections characterized by a linear θ–salinity relation (typically below about 500–800 m depth, Fig. 13a, b). In those depth sections Cu shows a negative deviation from linearity indicative of scavenging.

Generally Cu is strongly complexed with organic ligands in normal ocean surface waters, dramatically reducing the free ionic Cu concentration to much less than 1 pM (COALE and BRULAND, 1988; SUNDA and HANSON, 1987; HANSON *et al.*, 1988). It was shown that the degree of organic complexation rapidly decreased vertically, by three orders of magnitude over the first kilometer. In upwelling waters the degree of organic Cu complexation is likely to be relatively modest. For instance, the ensuing high free ionic Cu concentrations may suppress plankton growth, for instance because of competition with an essential micronutrient such as Mn (SUNDA and HUNTSMAN, 1983). Barber has reported experiments in which chelators added to upwelled water increased phytoplankton growth (BARBER and RYTHER, 1969; BARBER *et al.*, 1971). Although inconclusive the effects of added chelator have been attributed to the binding of Cu and the reduction of its free ionic activity.

CONCLUSIONS

1. The distributions of Cd, Zn, Ni and Cu are not influenced by the low oxygen conditions prevailing in intermediate waters in the Northwest Indian Ocean.

2. The vertical distribution of Cd at first sight resembled that of phosphate. For deep waters the Cd/phosphate slope is however significantly higher than the assumed global 0.35 nM/μM. From a comparison of literature data including our own it is evident that the consensus of a uniform global slope must be abandoned and needs to be refined.

3. The vertical distribution of Zn resembled that of silicate. There is a strong need for more reliable Zn data, especially in surface waters.

4. The vertical distribution of Ni resembled that of silicate. From a comparison of literature data including our own it is clear that the concept of a combined relation of Ni with phosphate (surface waters) and silicate (deep waters) is not globally valid and need be studied more closely.

5. Cu showed evidence of inputs in surface and bottom waters, scavenging throughout the water column, especially in surface waters at the two inshore stations and regeneration in deep waters. A good correlation with silicate is found for deep waters.

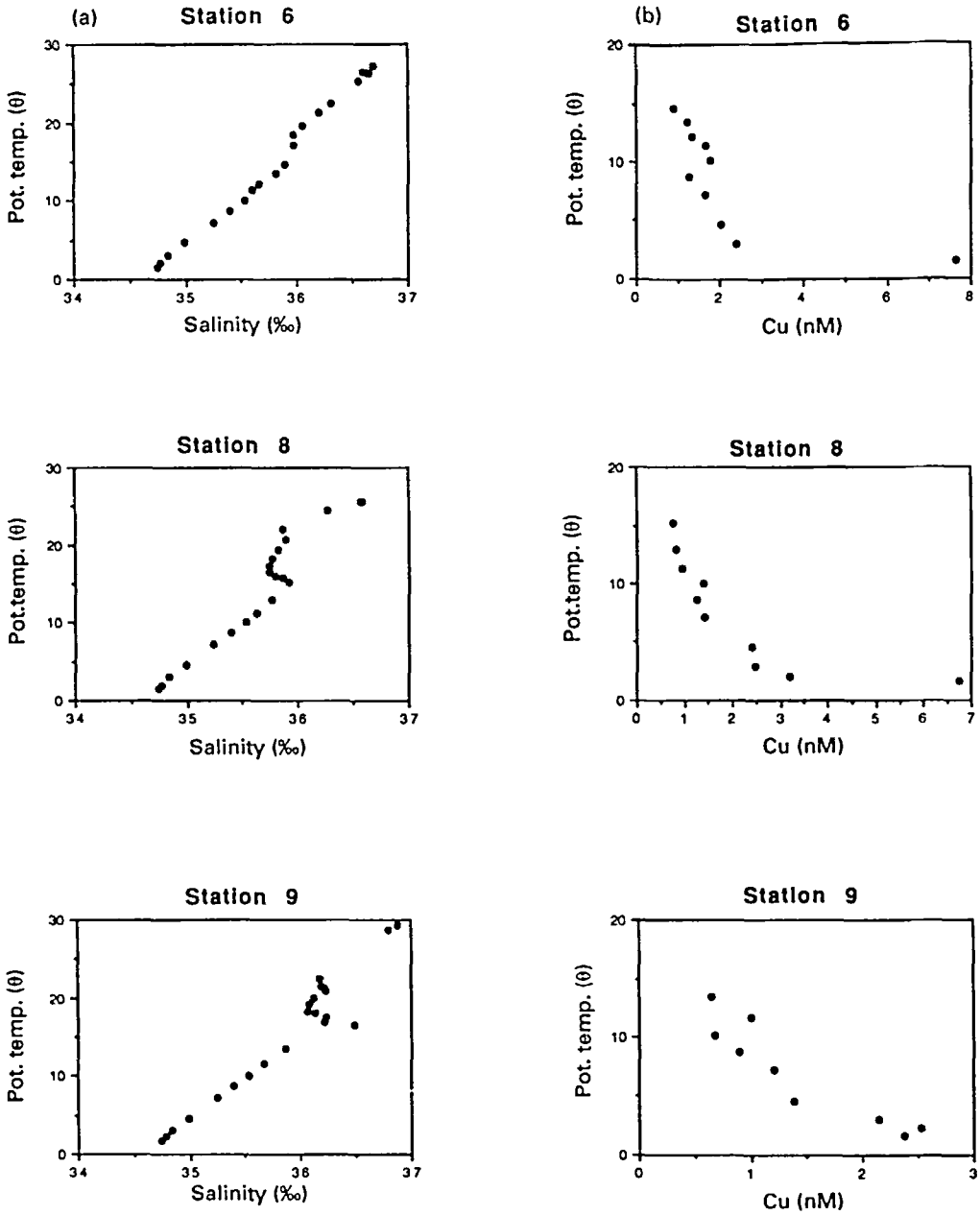


Fig. 13. (a) Potential temperature (θ) vs salinity at Stas 6, 8 and 9. (b) Potential temperature (θ) vs dissolved Cu for those deep waters having a linear potential temperature–salinity relationship at Stas 6, 8 and 9.

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